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DIELECTRIC CONSTANTS OF COMMERCIAL CASHEW SHELL OILS

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(*Received for publication, Nov. 12, 1949*)

ABSTRACT For the first time the dielectric constants of commercial cashew shell oil and its constituents have been studied. The investigations carried out on seven commercial samples reveal that the behaviour with temperature of the dielectric constants of the three main constituents of the oil, the sodium bicarbonate insolubles, the sodium bicarbonate solubles and the neutrals is widely different from one another and typical of each.

The differences in the dielectric constant-temperature curves of the oils and the bicarbonate insolubles are attributed to the viscosity effects due to the presence of self-polymerised products depending on the pre-treatment given to the oil during extraction, and to the considerable variation in the proportion of anacardol (decarboxylated anacardic acid) in the oils and their bicarbonate insolubles.

INTRODUCTION

It is an established fact that the dielectric constant of a substance is not a mere insignificant physical property but has a very great bearing on molecular structure. A study of the dielectric properties of the oils is interesting and informative from more than one aspect. There are a number of naturally occurring oils (triglycerides) whose chemical structures are sufficiently well established. In such cases a study of dielectric constant and dipole moments would enable one in probing into the molecular structure of the constituents of the oil. On the other hand the data on dielectric constants might be used in identifying the oil or establishing its purity. It is also interesting to follow up by means of dielectric constant studies some important physical and chemical changes which occur, for example, when the oil is gradually oxidised, heat bodied, or reacted to form polymers of various degrees etc. An exhaustive study of the dielectric constants as a function of temperature and frequency enables one to assess the insulating and dielectric properties of the varnishes or enamels of which the oil might form an important constituent.

All the oils that have been studied so far belong to the general category of triglycerides. A feature of the present paper is that for the first time the dielectric constant of an oil which is not a triglyceride, but essentially a mixture of phenolic bodies, have been determined. Another special feature about the present investigation is that a careful study has been made to find

out as to how the dielectric properties of an oil vary with the source, method of extraction and the extent of the initial processing. In the present work, the constituents of the oil have been seperated and their dielectric properties have been studied.

Stoops (1931) made the first significant contribution to the study of dielectric constants of oils. He determined the dielectric constants and densities of tung, linseed and castor oils over a wide range of temperature, (−70 to 100°C) and in dilute solutions of benzene and concluded that "probably all the animal and vegetable oils and fats of this class have moments between 2.7 to 3.7."

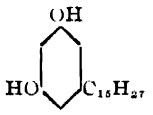
Paranjpe and Deshpande (1935) and Bhattacharya (1936) have measured the dielectric constants of various vegetable oils Electric moments in dilute benzene solutions have been evaluated and interpreted on the basis of molecular structure.

Caldwell and Payne (1941) undertook the investigation of the dielectric properties of a number of vegetable oils with the purpose of (*a*) determining as to what extent the dielectric constant, molar polarisation or effective dipole moment could be employed as means of identifying various drying oils and mixtures thereof and (*b*) investigating the effect of degree of heat bodying on the dielectric constant, molar polarisation and effective dipole moments of these oils.

Hazlehurst (1943) described the measurement of dielectric constant of raw, polymerised and oxydised linseed oils and showed how the absorption of oxygen and subsequent oxidation of the oil could be followed by the measurement of dielectric constants at different frequencies It has been claimed that as a result of this study of linseed oil, products which compare more than favourably with dehydrated castor oil have been prepared.

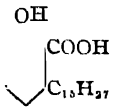
EXPERIMENTAL

The review of the literature has revealed that most of the work on the dielectric constants of oils has been made only on the triglycerides like castor oil, linseed oil, oiticica oil, perilla oil, tung oil, etc. Unlike other oils which are glycerides, cashew shell oil is completely phenolic in nature. It has been shown that the liquid contains two phenols. Approximately 10 per cent of the oil is present as cardol which is a substituted resorcinol of the following formula.

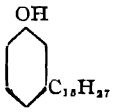


The substituent group is a linear chain, containing two double bonds, the position of which has not yet been determined.

The major constituent of the cashew shell oil is a salicylic acid dervative to which has been given the name anacardic acid. It has the following constitution:



The same substituent group which has been found in cardol is present in anacardic acid. Anacardic acid decarboxylates smoothly on thermal treatment to give a monohydric phenol known as anacardol of the formula :



The dielectric study of such a phenolic oil has not been undertaken so far. Cashew shell oil is very much used in insulating varnish and it makes an interesting study to find out the dielectric properties of the oil as well as its chief constituents Commercial oils from various sources extracted under varying conditions (heat treatment, solvent extraction, etc.) have been chosen for the study to find out whether all the oils are similar in behaviour so far as the dielectric properties are concerned. Such a study becomes interesting in view of the fact that cashew shell oil is known to vary in composition depending on the source and method of extraction (*c f.* Table I).

Materials.—The following seven typical samples with the respective compositions mentioned have been studied. Of these, two samples were solvent extracted from commercial shells, while the rest were typical commercial oils.

A novel and thorough method of investigating the types of constituents present in the various commercial specimens has been adopted in this paper. The method consists in extracting each of the commercial oils with dilute alkali so as to dissolve the phenolic and acidic portion and enabling the neutral body to be extracted with a suitable solvent. The alkali solution is next saturated with carbon dioxide to liberate the purely phenolic part of the oil from carboxylic portion, extracting the former again with a suitable solvent. Each commercial oil is separated into a neutral, acidic (sodium bicarbonate soluble), and phenolic (sodium bicarbonate insoluble) portion; and their dielectric properties have been studied. Table I gives an analysis

of the various commercial samples of cashew shell oil obtained from different producing centres.

TABLE I

Analysis of various samples of commercial oil.

Sample	Neutrals %	Bicarb. soluble %	Bicarb insolubles. %
Benzene extracted roasted shell (*Mangalore*)	2.0	5.0	93.0
Cardol corporation (*Mangalore*)	15.0	5.0	80.0
Pierce Leslie & Co. (*Calicut*)	1.0	3.0	96.0
Stanes & Co. (*Coimbatore*)	1.5	3.4	95.0
Fernandes Bros. (*Mangalore*)	2.0	6.0	92.0
Alcohol extracted roasted shell (*Mangalore*)	2.0	6.0	92.0
Naik & Co. (*Kassergaud*)	3.0	2.5	94.5

All the commercial samples of the oil have been obtained by drastic thermal treatment resulting in some polymerisation. The materials used represent the standard grade of industry available in India. No additional purification, except filtration and drying under vacuum for the removal of moisture, was made because it was desired to relate the results to actual industrial practice.

Apparatus.—The mostly widely used method of measuring the capacity of a condenser, first empty and then filled with the material, was employed to obtain the dielectric constants.

A very simple circuit similar to the one used by Nagmani and Jatkar (1942) was used for the measurement of capacities.

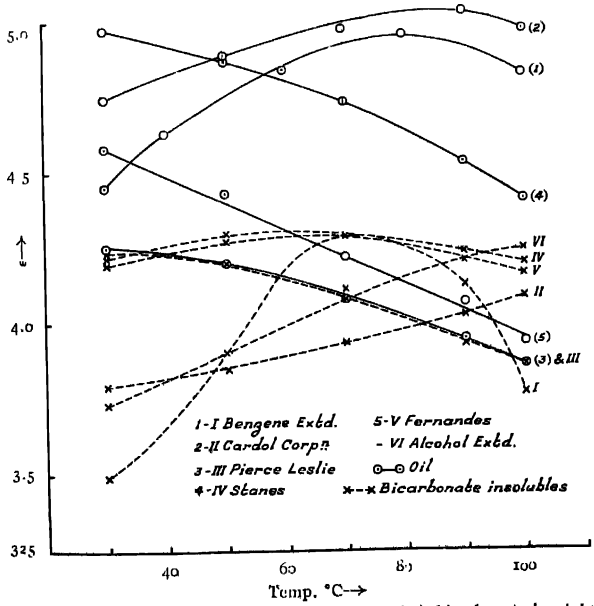
RESULTS

Table II gives the dielectric constants of various samples of cashew shell oil.

TABLE II

No.	Sample of cashew shell oil	ε	
		30°C	100°C
1.	Pierce Leslie & Co (Calicut)	4.26	3.87
2.	Benzene extracted (Laboratory)	4 45	4.84
3.	Fernandes Bros (Mangalore)	4 58	3 95
4.	Cardol Corpn. (Mangalore)	4.73	4.99
5.	Naik & Co (Kassergaud)	4.77	—
6	Stanes & Co. (Coimbatore)	4 97	4.12
7.	Alcohol Extracted (Laboratory)	6.00	—

The dielectric constants of the oils have been arranged in order of decreasing viscosity.



Dielectric constants of cashew shell oils and their bicarbonate insolubles

FIG. 1

In Table III comparative dielectric coustants of vegetable oils obtained by various experimenters are enlisted.

TABLE III

No.	Name of the oil	Temp in °C	ϵ	Frequencies
1	Cashew shell oil (author)	30	4 60 (average)	800 k c
2.	Castor oil (2)	34	4·55	1 k c.
	Castor oil (1)	30	4 54	300-1000 k c
	Castor oil (5)	26	4·45	10,000 k.c.
	Castor oil (3)	25	3 96	45-60 M.c.
3	Cocoanut oil (2)	34	3.41	1 k c,
	Cocoanut oil (5)	26	3 25	10,000 k.c.
4.	Dehydrated Castor oil (3)	25	3.03	45-60 M.c.
5.	Linseed oil (3)	25	3 20	60 c.
	Linseed oil (2)	34	3 30	1 k c.
	Linseed oil (4)	30	3.23	200 k.c
	Linseed oil (1)	30	3.35	300-1000 k c.
	Linseed oil (3)	25	3 17	45-60 M.c
6	Olive oil (2)	34	3.15	1 k.c.
	Olive oil (5)	26	3.25	10 000 k c.
7.	Oiticica oil (3)	25	6 14	60 c.
	Oiticica oil (3)	25	4·22	45-60 M.c
8.	Poppy seed oil (2)	34	3 55	1 k c.
9.	Perilla oil (3)	25	3.54	60 c.
	Perilla oil (3)	25	3.23	45-60 M.c.
10	Rapeseed oil (2)	34	3 08	1 k.c.
11.	Sesame oil (2)	34	3 16	1 k.c.
	Sesame oil (5)	26	3 37	10,000 k.c.
12.	Tung oil (1)	30	3 33	300-1000 k.c
	Tung oil (3)	25	3·34	60 c.
	Tung oil (3)	25	3.13	45-60 M.c.

(1) Stoops (1931) (2) Bhattacharyya (1936) (3) Caldwell and Payne (1941)
(4) Hazlehurst (1943) (5) Paranjpe and Deshpande (1935)

DISCUSSION

Table II shows that the dielectric constants of different commercial samples of cashew shell oil vary from one another (4.25 to 6 at 30°C and 3.87 to 4.99 at 100°C). The value for the alcohol extracted oil is unusually high. This may be due to (*a*) some resinous constituent dissolved in the oil (*b*) due to traces of some alcohol retained in the oil in spite of vacuum distillation after dissolving the extracted oil in benzene. In view of its high dielectric constant the presence of even a small quantity of ethyl alcohol ($\epsilon = 25$ at 25°C) could easily be responsible for the observed high value of the dielectric constant of the alcohol extracted oil. In many cases the dielectric constants is still in the increasing trend at 30°C. Hence the dielectric constants at 100°C have been tabulated in order to eliminate the dispersion effect. It is seen from Fig. 1 that at 100°C the dielectric constants are in the falling region. The dielectric constant at room temperature is found to increase with decrease in the viscosity of the sample.

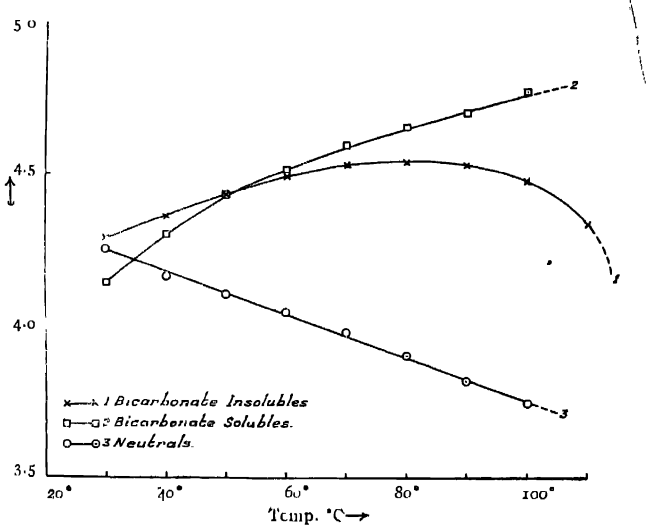
The available data on the dielectric constants of all the vegetable oils studied so far have been tabulated in Table III. It is interesting to see that all the other oils, except castor and oiticica oils, have a decidedly lower dielectric constant than cashew shell oil at room temperature and near about the frequencies used in the present investigation. Castor oil and oiticica oil show anomalous dispersion. The dispersion of cashew shell oil has been studied by varying the temperature but maintaining a fixed frequency for measurement (c.f. Fig. 1). It may be mentioned here that the dielectric dispersion can be studied by two alternative methods: (1) By varying the frequency but maintaining a constant temperature, (2) By varying the temperature at a fixed frequency. The latter method has been employed in the present study. It is well known from the behaviour of the molecule in an electrical field that the dielectric constant-temperature curve should attain a maximum after an initial increase with temperature and finally should follow a gradual and continuous fall.

At very low temperatures there is very little orientation of the molecules due to increased viscosity which results in a low dielectric constant. With increase in temperature, polarisation increases owing to enhanced orientation of molecules. This is responsible for the gradual initial rise of dielectric constant with temperature. With further rise in temperature forces due to thermal agitation become predominant and consequently the number of oriented molecules diminish resulting in a lower dielectric constant. The results of our studies on the temperature coefficient of the dielectric constants of the various commercial cashew shell oils and their constituents fully conform with the above picture. These curves (Fig. 1) are similar in nature to those obtained by Bhattacharya (1944) for lac and Mead and Fuoss (1941) and Dakin (1943) for vinyl chloride and vinyl acetate and are typical of the behaviour of viscous liquids in an electrical field. The maximum

dispersion is shown by the alcohol extracted sample whose dielectric constant varies from 6.00 at 30°C to 7.1 at 80°C.

Cardol and benzene extracted samples also show dispersion but on a smaller magnitude. From the curves (1,2) of the above oils it is obvious that the dielectric constant is very near the static value at 100°C at which point the dielectric constant—temperature curve has already started falling with increase in temperature. The other samples (3, 4 and 5) do not show any dispersion in the temperature region studied.

The dielectric properties of the constituents of cashew shell oil separated according to the new scheme have been studied and the results are plotted in Fig. 2. In the first instance the individual constituents obtained from different samples have been mixed together and their dielectric properties investigated.



Dielectric constants of constituents of cashew shell oil

FIG. 2

The behaviour of the dielectric constants of the three constituents with temperature is widely different from one another and typical of each. The curve for bicarbonate solubles shows a continuous increase with temperature even up to 100°C. This behaviour is typical of a carboxylic acid like benzoic acid.

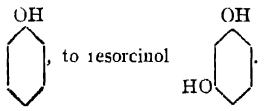
This abnormal increase with temperature may be either due to dispersion effects or the molecular association. In view of the fact that bicarbonate solubles are less viscous than the oils, such a large dispersion effect is not probable. It has been shown that benzoic and other carboxylic acid molecules

associate to form dimers. The observed gradual increase in dielectric constant may be due to gradual dissociation of dimers of anacardic acid with increase in temperature.

Bicarbonate insolubles, the major constituent of the oils behave much like the oil as regards the variation of dielectric constant with temperature. The neutrals which form a negligible portion of the oil have a lower dielectric constant with a negative temperature coefficient

A comparative study of the dielectric constant—temperature curves of the oils and their bicarbonate insolubles shows (Fig. 1) that in the case of Cardol Corporation oil, benzene extracted oil and Stanes oil, the curves for the bicarbonate insolubles fall much below those of the respective oils. This is due to the higher viscosity of the bicarbonate insolubles as compared with these oils. In the case of Fernandes oil, the curves cross near 60°C. At lower temperature (30–60°C) the Fernandes oil has a higher dielectric constant than the bicarbonate insolubles while after 60°C the situation is just the reverse. This means that though initially the viscosity forces are stronger in the case of the bicarbonate insolubles, the decrease in viscosity of the bicarbonate insolubles with temperature is so high that at higher temperatures the viscosity forces of the bicarbonate insolubles exert a lesser influence than that of the oils. For the Pierce Leslie oil both the curves go hand in hand. In the case of Pierce Leslie sample, evidently the viscosity of both are of the same magnitude. In the case of the alcohol extracted sample the difference in behaviour between the bicarbonate insolubles and the oil is enormous. Though in both cases the dielectric constant is still in the increasing trend in the range of temperature studied, yet the values for the oil are progressively very much higher than that of bicarbonate insolubles. All the anomaly between the dielectric behaviour of the oils and their bicarbonate insolubles are, as has been explained above, due to the viscosity effects. It will be, however, interesting to find out as to what exactly is responsible for these differences in viscosity between the oils and the bicarbonate insolubles. It is a well-known fact that cashew shell oil polymerises with heat and in this process the viscosity of the oil is increased. It is not yet established as to how the heat polymerisation of the oil occurs, and the mechanism of polymerisation is still to be understood. It is this polymer that is responsible for the high viscosity of the oil and its constituents. Comparatively, however, the oil is less viscous in that it is diluted by the relatively mobile solubles, (anacardic acid) and the neutrals. Again due to the differences in the extent of initial heat treatment and the method of extraction of samples the degree of polymerisation varies from sample to sample. This explains the difference in the magnitude of the anomalies that exist between the viscosity and the nature of the dielectric constant—temperature curve for the oils and the bicarbonate insolubles.

There is one more point which requires careful study and consideration. The bicarbonate insoluble portion of the oil is known to consist essentially of two main constituents: (1) anacardol derived from anacardic acid by decarboxylation and (2) cardol which is existing in the original oil. A comparative study of the dielectric constants of cardol and anacardol has not so far been undertaken for the very simple reason that it has not been possible to separate them from a mixture. Structural considerations would, however, indicate that their dielectric constants would be related to each other, at least qualitatively, in the same manner as that of the structurally analogous phenol



, to resorcinol .

The essential difference between the two sets of compounds is the fact that 'H' of the latter is replaced by the nonpolar $C_{15}H_{27}$ in anacardol and cardol. Phenol has a dielectric constant of 8.02 at 113°C and resocinol 14.5 at 110°C., (Kulkarni 1948). It is evident from this that the introduction in the phenol molecule of a 'OH' group in the meta position results in a marked increase in the dielectric constant. On the same analogy one could expect that the 'm' dihydroxy phenol, cardol should have a decidedly higher dielectric constant than that of the monohydroxy phenolanacardol. Hence the dielectric constant of the binary system, cardol—anacardol, would depend on the proportion of the individual constituents present. Consequently the magnitude of the dielectric constant of the oil or the bicarbonate insolubles would be, to a great extent, a function of the relative proportions of cardol and anacardol present in the sample under consideration. A study of the literature reveals the diversity of the composition of the raw cashew shell oil.

TABLE IV

Author	Percentage of anacardic acid
Joseph et al (1922)	90
Patel and Patel (1935)	40
Pillay (1935)	90
Backer and Haack (1941)	67

It is seen from Table IV that the percentage of anacardic acid of raw oil varies right from 40 to 96. The lowest value of 40 percent is not very reliable in that Patel and Patel have arbitrarily assumed the yield of oil as 33⅓ percent. Still Backer and Haack have given a value of 67 percent which is far less than the often quoted literature value of 'about 90%.' The consequence of such a wide variation in the percentage of anacardic acid in the raw oil is that the percentage of anacardol (which is anacardic acid decarboxylated) in the commercial oil is subject to correspondingly large variations depending on the source. Thus the dielectric constant of the oil or the bicarbonate insolubles is a function of its anacardol content which again depends on the source of the oil.

Hence in addition to the viscosity effects caused by the heat polymerised products the variation of the percentage of anacardol in the oil or in the bicarbonate insolubles could also be responsible for the differences in the dielectric behaviour of the different oils and their constituents. In other words each of the sample of the oil and its constituent is characterised by its dielectric behaviour depending upon (1) viscosity which is a function of the amount of polymerized product present and (2) its anacardol content, which varies from source to source.

In view of the above observations it is obvious as to how futile it is to speculate on a stray reading of dielectric constant of a sample of a particular oil The influences governing the dielectric behaviour are many and varied and the exhaustive studies made in ths present work on cashew shell oil clearly illustrate the valuable features of this point. It would be very interstring to study the dielectric properties of other oils with a view to finding out as to how factors like the source methods of extraction and pre-treatment influence the dielectric properties.

ACKNOWLEDGMENT

Thanks of the authors are due to Prof. P. Ramaswami Ayyar, M.A. for his helpful suggestions during this work.

The authors are indebted to Dr. S K. K. Jatkar, D Sc for having provided facilities for conducting this research

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